Cyclooctatetraene Palladium (II) Bromide;
Synthesis and Characterization
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Many complexes of transition metal ions with cyclo-
octatetraene have been reported, but there is no record of the preparation of cyclooctatetraene palladium (II) bromide. In 1953, Jensen¹ prepared cyclooctatetraene platinum (II) chloride from sodium tetrachloroplatinate (II) and cyclooctatetraene using water as solvent; the method may also be used for the corresponding bromide. Kharasch, Seyler, and Mayo² reported preparation of certain olefin-palladium (II) chloride complexes by means of the reaction of an olefin such as cyclohexene, styrene, or ethylene with bis (benzonitrile) palladium (II) chloride. This method has been modified by Kuljian and Frye³ and used in the present research to prepare bis (benzonitrile) palladium (II) bromide, both unreported compounds.

Experimental
Preparation of bis (benzonitrile) palladium (II) bromide

Two grams of palladium (II) bromide was dissolved in fifty milliliters of aniline free benzonitrile with prolonged heating at 100 °C. The resulting solution was filtered while hot through a Buchner funnel and was allowed to cool. Dark brown crystals of bis (benzonitrile) palladium (II) bromide were recovered. The remaining solution was diluted with either cyclohexane or low boiling petroleum ether to precipitate more crystals. The mixed crystals were vacuum filtered, washed with petroleum ether, and desiccated at atmospheric pressure over Drierite: reduced pressure tends to ‘pump off’ benzonitrile. Yield was 3.2 grams, or about 90 per cent. Attempts to increase the yield by dilution with petroleum ether resulted in precipitation of palladium (II) bromide; less benzone cannot be used because the benzonitrile complex would not then dissolve completely.

Cyclooctatetraene palladium (II) bromide is soluble in acetone, chloroform, benzene, methanol, and glacial acetic acid; it is insoluble in diethyl ether and reacts with dimethylformamide, dimethyl sulfoxide, and excess benzonitrile. The compound was characterized by comparison of the infrared spectrum with that of cyclooctatetraene palladium (II) chloride as reported by Fritz and Keller⁴. Carbon-hydrogen data are given in Table I:

<table>
<thead>
<tr>
<th>% C</th>
<th>% H</th>
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<tbody>
<tr>
<td>25.94</td>
<td>2.14</td>
</tr>
</tbody>
</table>

Table I. Data on carbon-hydrogen analysis of cyclooctatetraene palladium (II) bromide.

Table II lists ultraviolet-visible absorption data for cyclooctatetraene palladium (II) bromide; data is included for the chloride for comparison:

<table>
<thead>
<tr>
<th>wavelength, millimicrons</th>
<th>cyclooctatetraene palladium (II) bromide</th>
<th>cyclooctatetraene palladium (II) chloride</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>432</td>
<td>370</td>
</tr>
<tr>
<td>molar absorptivity x 10⁻³</td>
<td>7.4</td>
<td>2.0</td>
</tr>
</tbody>
</table>

Table II. Ultraviolet-visible spectral data.

¹ K. Jensen, Acta. chem. scand. 7, 868 [1953].
² M. Kharasch, R. Seyler and F. Mayo, J. Amer. chem. Soc. 60, 882 [1938].
⁴ H. Fritz and H. Keller, Chem. Ber. 95, 158 [1962].